

THE CALCULATION OF VELOCITY OF SOUND FOR MOLECULAR CRYSTALS¹

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¹Paper presented at the Fourteenth Symposium on Thermophysical Properties, June 25-30, 2000, Boulder, Colorado U.S.A.

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ABSTRACT

The paper deals with a mathematical model for the calculation of thermodynamic properties of solids. The mathematical model, based upon statistical thermodynamics, is designed to assess the impact of atom vibration, electron excitation and the effect of intermolecular energy between atoms in a crystal. To calculate the configuration integral the perturbation theory was used with the van der Waals model as perturbation. The temperature-variable coefficients were introduced into the model presented in this paper. Finally, the model was compared with the experimental data proving a good matching.

KEY WORDS: thermodynamics of solids, molecular crystals, velocity of sound, perturbation theory

1. INTRODUCTION

The need for mathematical modeling of thermodynamic properties of state arises in various fields. Currently, a growing emphasis is placed on new materials, such as different alloys, polymers, plastic material and ceramics [1,2]. Due to a large number of possible combinations of various components mathematical models are frequently used to predict thermodynamic properties. Mathematical modeling is often used also in some metallurgical processes, such as sintering, corrosion, welding.... Furthermore, analytical computation of thermodynamic properties of state in solids is of paramount importance also in a number of other fields such as planetary physics, for example. Another important area is the production of liquid-solid, solid-gaseous phase diagrams [3]. At higher pressure and temperature bands such measurements may be very costly, which is why mathematical models are often used instead.

2. STATISTICAL THERMODYNAMICS OF SOLIDS

Assume that each form of motion is independent of the others; thus, the energy of the system of molecules can be written as a sum of individual contributions or decoupled forms of motion:

- a) Vibration energy of molecules (vib) due to the relative motion of atoms inside the molecules.
- b) Potential energy (pot) of a system of molecules, which occurs due to the attractive or repulsive intermolecular forces in a system of molecules.
- c) Energy of electrons (el), which is concentrated in the electrons or in the electron shell of an atom or a molecule
- d) Nuclear energy (nuc), which is concentrated in the atomic nuclei.

Writing down the energy of the ground state (0) as a sum of individual contributions of energies in the ground state for a system of molecules, we obtain:

$$E_0 = E_{\text{vib}_0} + E_{\text{el}_0} + E_{\text{nuc}_0} + \dots \quad (1)$$

The energy required to excite the system of molecules to higher energy levels is:

$$E = E_0 + E_{\text{vib}} + E_{\text{el}} + E_{\text{nuc}} + E_{\text{conf}} \quad (2)$$

– potential intermolecular energy depends upon the position of nuclei in the space
 – we neglect the influence of the orientation of a molecule in the space,
 – we assume that the intermolecular energy of the system of molecules is an additive property,

– since in the presented model the phenomena treated are at higher temperatures, where quantum effects have a very low influence, we used classical statistical thermodynamics to compute the thermodynamic properties of state of one-, two- or multi-atom molecules. To this end, we can use the canonical partition [4], which deals with the system of particles with the final number of particles N , the temperature T and the volume V .

Now introduce the term of partition function Z [5,6], which applies to the system of particles at a certain volume V , temperature T and particle number N .

Assuming that the energy spectrum is continuous and having the above assumptions we can then write the canonical partition function for the one-component system in an even easier manner:

$$Z = \frac{1}{N! h^{Nf}} \int \dots \int \exp\left(-\frac{E_{\text{vib}} + E_{\text{el}} + E_{\text{nuc}}}{k_B T}\right) d\vec{p}_1 \cdot d\vec{p}_2 \dots d\vec{p}_N \cdot \times \int \dots \int \exp\left(-\frac{E_{\text{pot}}}{k_B T}\right) d\vec{r}_1 \cdot d\vec{r}_2 \dots d\vec{r}_N \quad (3)$$

The second term on the right-hand side in Eq. (3) is called the configurational integral, f is the number of degrees of freedom of an individual molecule.

Similarly, we can write down also the partition function Z for a multi-component system of indistinguishable molecules:

$$Z = \frac{1}{\prod_i N_i! h^{N_i f_i}} \int \dots \int \exp\left(-\frac{E_{\text{vib}} + E_{\text{el}} + E_{\text{nuc}}}{k_B T}\right) d\vec{p}_1 \cdot d\vec{p}_2 \dots d\vec{p}_N \cdot \\ \times \int \dots \int \exp\left(-\frac{E_{\text{pot}}}{k_B T}\right) d\vec{r}_1 \cdot d\vec{r}_2 \dots d\vec{r}_N \quad (4)$$

In Eq. (4) N_i is the number of molecules of the i -th component, f_i is the number of degrees of freedom of the i -th molecule. On the basis of all indicated generalizations we can write, using the canonical partition, the partition function Z of the one-component system as a product of partition functions:

$$Z = Z_0 Z_{\text{vib}} Z_{\text{el}} Z_{\text{nuc}} Z_{\text{conf}} \quad (5)$$

For a system of many components the partition function Z [1,7,8] can be written as a product of partition functions for individual terms:

$$Z = \prod_i (Z_0 Z_{\text{vib}} Z_{\text{el}} Z_{\text{nuc}})_i Z_{\text{conf}} = \prod_i Z_i Z_{\text{conf}} \quad (6)$$

By means of the partition function Z the canonical theory allows the computation of thermodynamic properties of state [9-11]:

$$\begin{aligned} \text{pressure: } p &= k_B T \left(\frac{\partial \ln Z}{\partial V} \right)_T, & \text{internal energy: } U &= k_B T^2 \left(\frac{\partial \ln Z}{\partial T} \right)_V, \\ \text{free energy: } A &= -k_B T \ln Z, & \text{entropy: } S &= k_B \cdot \left[\ln Z + T \cdot \left(\frac{\partial \ln Z}{\partial T} \right)_V \right], \\ \text{isochoric heat per mole: } C_v &= 2k_B T \left(\frac{\partial \ln Z}{\partial T} \right)_V + k_B T^2 \left(\frac{\partial^2 \ln Z}{\partial T^2} \right)_V. \end{aligned} \quad (7)$$

3. VELOCITY OF SOUND

Using Eq. (7) we can calculate also some derived thermodynamic properties of state, such as velocity of sound. Velocity of sound is the velocity of the propagation of longitudinal sound waves. The calculation of the velocity of sound is very important primarily in the measuring systems, such as in acoustic measuring devices of the level of the cooling medium. In most processes the assumption on isentropic velocity of sound is a sufficiently good approximation. In some processes, such as the process of dissociation and ionisation, the assumption on isothermal velocity of sound is closer to the real state.

$$\text{Isentropic velocity of sound: } c_{0S} = \sqrt{-V^2 \left(\frac{\partial p}{\partial V} \right)_{S,\psi} \cdot \frac{1}{M}} \quad (8)$$

$$\text{Isothermal velocity of sound: } c_{0T} = \sqrt{-V^2 \left(\frac{\partial p}{\partial V} \right)_{T,\psi} \cdot \frac{1}{M}} \quad (9)$$

4. VIBRATION PROPERTIES OF SOLIDS

Our thermodynamic system consists of N particles associated by attractive forces. Atoms in a crystal lattice are not motionless but they constantly thermally oscillate around their positions of equilibrium. At temperatures far below the melting point the motion of atoms is approximately harmonic [10,11]. This assembly of atoms has $3N-6$ vibration degrees of freedom. Ignore 6 vibration degrees of freedom and mark the number of vibration degrees of freedom with $3N$.

Through the knowledge of independent harmonic oscillators the distribution function Z [10] can be derived as follows:

$$Z = \left[\frac{\exp\left(-\frac{h\nu}{2k_B T}\right)}{1 - \exp\left(-\frac{h\nu}{k_B T}\right)} \right]^{3N} \quad (10)$$

In Eq. (10) ν is the oscillation frequency of the crystal. The term $h\nu/k$ is the Einstein temperature θ_E .

In comparing the experimental data for simple crystals a relatively good matching with analytical calculations at higher temperatures is observed whereas at lower temperatures the discrepancies are higher. This is why Debye corrected the Einstein's model by taking account of the interactions between a number of quantized oscillators [10,11,12]. Using the canonical distribution the partition function [11] may be written as:

$$\ln Z = -\frac{9}{8} N \frac{\theta_D}{T} - 3N \cdot \ln \left(1 - \exp\left(-\frac{\theta_D}{T}\right) \right) + 3N \frac{T^3}{\theta_D^3} \int_0^{\theta_D/T} \frac{\xi^3}{\exp(\xi)-1} d\xi \quad (11)$$

In Eq. (11) θ_D is the Debye temperature: $\theta_D = \frac{v_{\max} h}{k}$. By developing the third term in

Eq. (11) into a series for a higher temperature range [13] we can write:

$$\frac{\xi^3}{\exp(\xi)-1} = \xi^2 - \frac{1}{2}\xi^3 + \frac{1}{12}\xi^4 - \frac{1}{720}\xi^6 + \dots \quad (12)$$

Using Eq. (12) Eq. (11) turns into the following expression:

$$\ln Z = -\frac{9}{8} N \frac{\theta_D}{T} - 3N \cdot \ln \left(1 - \exp\left(-\frac{\theta_D}{T}\right) \right) + 3N \left(\frac{T}{\theta_D} \right)^3 \left[\frac{1}{3} \left(\frac{\theta_D}{T} \right)^3 - \frac{1}{8} \left(\frac{\theta_D}{T} \right)^4 + \frac{1}{60} \left(\frac{\theta_D}{T} \right)^5 - \frac{1}{5040} \left(\frac{\theta_D}{T} \right)^7 + \frac{1}{272160} \left(\frac{\theta_D}{T} \right)^9 - \dots \right] \quad (13)$$

The relation between the Einstein and Debye temperature may be written as¹²⁻¹⁵:

$$\theta_E = (0.72 \dots 0.75) \theta_D. \quad (14)$$

The Debye characteristic temperature was determined by means of the Grüneisen independent constant γ :

$$\theta_D = CV^{-\gamma}, \quad (15)$$

where C is constant dependent on material.

We developed a mathematical model for the calculation of thermodynamic properties of polyatomic crystals. The derivations of the Einstein and Debye equations, outlined in the previous paragraphs, apply specifically to monoatomic solids, i.e. those belonging to the cubic system. However, experiments have shown that the Debye equation represents the values of specific heat and other thermophysical properties for certain other monoatomic solids, such as zinc, which crystallizes in the hexagonal system. Suppose that the crystal contains N molecules, each composed of s atoms. Since there are Ns atoms, the crystal as a whole has $3Ns$ vibrational modes. A reasonable approximation is obtained by classifying the vibration into

- a) $3N$ lattice vibrations, which are the normal modes discussed in the Debye treatment (acoustical modes).
- b) Independent vibrations of individual molecules in which bond angles and lengths may vary. There must be $3N(s-1)$ of these (optical modes). We expressed the optical modes using the Einstein model.

5. INFLUENCES OF ELECTRONS

5.1 Electronic Gas in Metals

We are interested in electrons capable of moving in a crystal and not belonging to any individual atoms but entirely to the crystal. Such are, for example, conduction

electrons in metals. A number of such electrons may be called electronic gas. Using the Fermi-Dirac statistics the configuration integral [9,10,11,12,13] may then be calculated for temperatures lower than the Fermi temperature:

$$T_F = \frac{\epsilon_F}{k_B} \quad (16)$$

For metals the Fermi temperature is a few thousand kelvins. In Eq. (26) ϵ_F is Fermi energy.

$$A_{el} = \frac{3}{5} N \epsilon_F \left(1 + \frac{5\pi^2}{12} \left(\frac{k_B T}{\epsilon_F} \right)^2 \right) - N k_B \frac{\pi^2}{2} \frac{k_B T^2}{\epsilon_F}. \quad (17)$$

5.2 Influence of Electron Excitation

To calculate the influence of electron excitation into excited states classical models of statistical thermodynamics may be used. The electron partition function for the technical range of temperatures and pressures can be written as follows:

$$Z_{el} = \left(g_{el(0)} + g_{el(1)} \cdot \exp \left(- \left(\frac{\theta_{el}}{T} \right) \right) \right)^N. \quad (18)$$

In Eq. (18) θ_{el} is electronic characteristic temperature, $g_{el(0)}$ and $g_{el(1)}$ are the degrees of degeneration of the basic and the first excited state.

6. CRYSTAL BONDS

The bonds between the atoms or molecules in a crystal are of electrostatic nature. They are based upon Coulomb's law of attractive and repulsive forces. Atoms are associated into a crystal if the total energy of the system is reduced. Roughly speaking, bonds may be classified into the following types:

a) Van der Waals bonds result from forces between inert atoms and mostly saturated molecules [5,9,11,12,14]. Van der Waals (VDW) forces appear due to time-varying dipole moments occurring due to a rapid motion of electrons. In solids this form of bond is rather rare. The system of molecules bound in this manner is called a molecular crystal, typical of some molecules such as CO_2 , CH_4 , NH_3 ... The properties of substances bound by means of the VDW bond are softness, low melting point and solvability in covalent liquids.

b) Ionic bonds occur due to interactions between ions of opposite charge, which results in an arranged three-dimensional structure

c) Covalent or strong bond is formed if one or more electrons are shared between two atoms

d) Metallic bond occurs in metallic crystals with external valence electrons relatively weakly bound to the nucleus of the atom.

e) Hydrogen bond, which plays an important role in ice, hydrates of salt, is formed in polar parts of molecules where hydrogen is present.

The analytical calculation of configuration integral in solids is a very difficult task. Most frequently numerical procedures are applied in practical computations by means of the Monte-Carlo method [8,13]. Nevertheless, the presented method requires a lot of computer time with another serious drawback being also that it does not provide a functional dependence of thermodynamic properties on temperature and volume. Empirical equations⁶ are frequently used as well, though mostly without any theoretical basis built on a molecular view of the world. In the paper presented we used the perturbation VDW theory for solids around the model of hard spheres [16,17,18] to calculate the thermodynamic properties of state. In order to calculate the mixtures of

atoms of hard spheres we obtain the configuration free energy for a certain binary crystal:

$$A_{\text{conf}0} = Nk_B T \left(-3 \ln \left(\frac{V^* - 1}{V^*} \right) + 5.124 \cdot \ln V^* - 20.78 V^* + 9.52 V^{*2} \right. \\ \left. - 1.98 V^{*3} + C_0 + \psi_1 \cdot \ln \psi_1 + \psi_2 \cdot \ln \psi_2 \right), \quad (19)$$

$$C_0 = 15.022, \quad V^* = \frac{V}{V_0}, \quad V_0 = \frac{N\sigma^3}{\sqrt{2}}$$

To calculate the perturbation contribution the VDW model was used. In most of the technical literature [16-18] the VDW model is treated only in relation to atomic structure, whereas we additionally presented the temperature-dependent coefficients.

$$A_{\text{conf}1} = - \frac{a(\psi_1, \psi_2, T)}{V}. \quad (20)$$

The configuration integral is thus formed by the contribution of hard spheres and perturbation:

$$A_{\text{conf}} = A_{\text{conf}0} + A_{\text{conf}1}. \quad (21)$$

In our case coefficient a was determined as a temperature-dependent polynome following a comparison between experimental data and analytical results:

$$a = a_0 + a_1 T + a_2 T^2. \quad (22)$$

Coefficients a_0 , a_1 , a_2 are obtained by numerical approximation and the comparison with thermodynamic data.

7. RESULTS AND DISCUSSION

The presented mathematical model was used to calculate thermodynamic properties of state of some solids, namely:

1. Copper (Cu), as a typical representative of metallic bond.
2. Sodium chloride (NaCl), as a typical representative of ionic bond.
3. Carbon dioxide (CO₂), as a typical representative of molecular crystals.

Tables 1,2, and 3 show the comparison between analytical calculations and experimental values [12,19]. Presented are the results of enthalpy, specific heat and velocity of sound.

The comparison of results showed a very good matching with experimental data, particularly for copper. Somewhat less optimum is the matching of analytical calculations with experimental data, such as NaCl and CO₂. The reason for such a higher discrepancy between the measured and calculated results lies in the complex structure of crystals composed of diverse atoms.

NOMENCLATURE

A	free energy
AAD	average absolute deviation
an.	analytical results
c _{0S}	isentropic velocity of sound
c _{0T}	isothermal velocity of sound
C _v	heat capacity at constant volume per mole
C _p	heat capacity at constant pressure per mole
E	energy
Exp.	Experimental results
f	number of degrees of freedom
g	degree of degeneration

H	enthalpy, Hamiltonian
h, \hbar	Planck constant
k_B	Boltzmann constant
M	molecular mass
N	number of molecules in system
p	pressure, momentum
S	entropy
T	temperature, kinetic energy
T_F	Fermi temperature
U	internal energy
V	volume, potential energy
Z	partition function
ν	oscillation frequency
ϵ_F	Fermi energy
θ_{el}	electronic temperature
θ_D	Debye temperature
θ_E	Einstein temperature
γ	Grüneisen constant

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TABLES

Table 1: Isentropic and isothermtal velocity of sound for copper

T	V	c_{0S} -an.	c_{0S} -exp.	c_{0T} -an.	c_{0T} -exp.
K	$10^6 \text{m}^3/\text{mol}$	m/s	m/s	m/s	m/s
250	7.04	3860	3859	3805.2	3807.4
300	7.06	3860	3838	3780.7	3775.8
500	7.12	3945	3754	3851.7	3651.4
800	7.26	3538	3668	3413.3	3515.3
1200	7.45	3687	3631	3395.8	3369.4
AAD		0.0215		0.0187	

Table 2: Isentropic and isothermal velocity of sound for sodium chloride

T	V	c_{0S} -an.	c_{0S} -exp.	c_{0T} -an.	c_{0T} -exp.
K	$10^6 \text{m}^3/\text{mol}$	m/s	m/s	m/s	m/s
125	26.60	3132	3382	3116	3356
150	26.60	3636	3378	3547	3345
175	26.70	3362	3380	3335	3335
250	26.90	3304	3368	3242	3299
290	27.00	3400	3366	3302	3278
AAD		.03694		.0313	

Table 3: Molar heat capacity at constant pressure and enthalpy for carbon dioxide

T	V	C _P -an.	C _P -exp.	H-an.	H-exp
K	10 ⁶ m ³ /mol	J/molK	J/molK	kJ/mol	kJ/mol
173	27.588	51	49,1	4,62	5,49
183	27.808	53,2	52,8	5,41	6,07
193	28.116	55,4	54,8	6,39	6,60
203	28.468	57,5	64	7,26	7,17
213	28.908	59,7	70,4	8,61	7,90
AAD		.062		0.081	